PREDICTING THE TRANSIENT DEVOLATILIZATION OF VARIOUS COALS WITH FLASHCHAIN

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INTRODUCTION

In coal-fired utility boilers, devolatilization generates the gaseous fuel compounds which ignite and stabilize the flame. Precursors to noxious gases are also released as the coal thermally decomposes. Pulverized coal injected into hot gases devolatilizes while it heats at 10^4 - 10^5 K/s. The process takes only several milliseconds, and is completed before the fuel reaches its ultimate temperature. The rank of coal largely determines the total amount of volatiles as well as the proportions of heavy aromatic tar compounds and noncondensible gases. Coal rank is also an influence on the reaction rate, albeit a poorly characterized one. Until very recently no reliable transient data were available for boiler conditions, although laboratory studies at slower heating rates indicated that low rank coals devolatilize significantly faster than bituminous coals.[1]

This study uses FLASHCHAIN[2-4] to demonstrate that continuous variations of only a handful of structural features in the coal and one rate constant underlie the transient devolatilization of coals across the rank spectrum. It shows that the ultimate analysis is the only sample-specific data needed for accurate predictions of ultimate tar and total yields with this theory, consistent with a previous parametric sensitivity study.[4] Lignites and low volatility coals are featured in this evaluation, to complement the emphasis on subbituminous and high volatile (hv) bituminous samples in the first evaluation.[4] This study extends earlier work further by identifying the parametric basis for reliable transient predictions for rapid atmospheric devolatilization of any coal type.

GUIDELINES FOR THE DATA CORRELATIONS AND MODEL PARAMETERS

Taken together, the two laboratory studies[5-6] selected for the model evaluation depict the behavior throughout the entire range of coal types, for wide ranges of temperature and heating rate at atmospheric pressure. Freihaut and Proscia used a wire-grid heater in which the sample was dispersed in a layer only a few particles deep, and assigned process temperatures after very extensively characterizing the vagaries of fine-wire thermocouples in such systems.[7] Their ultimate weight loss values and tar yields are based on heatup at 725 K/s, followed by 10s at the stated reaction temperatures. Transient weight loss is available for a heating rate of 800 K/s. Even though forced quenching was not implemented, their samples cooled at rates from 1500 to 2000 K/s, which is fast enough to virtually eliminate decomposition during cooling. However, their transient tar yields are too scattered to be used for model evaluations.

Chen and Niksa[7] used a novel radiant coal flow reactor to impart heating rates exceeding 10^4 K/s. Their calculated thermal histories, described elsewhere,[8] indicate a nominal heating rate of 15,000 K/s for the long-residence-time-cases considered here. The corresponding model predictions are based on transient heatup at this rate to 1300 K. Predicted tar yields are compared to the sum of the measured yields of tars and oils, consistent with the product recovery scheme in their study.

Collectively 14 different coal samples are represented. As seen in Table I, they represent nominal ranks from lignite to anthracite, and 40% of them are low volatility samples. Note also that in three cases, virtually identical samples were used in both laboratory studies. The atomic H/C and O/C ratios are based on the reported ultimate analyses. The additional structural and characterization data in Table I are needed to define FLASHCHAIN's input parameters. All values are based on regressions of literature values reported elsewhere.[2,4] So the only coal-specific input for these simulations is the ultimate analyses. Thus, this study will determine if samples having the same nominal rank but different O/C and H/C ratios can be distinguished with this theory, as suggested by a previous study of parametric sensitivity.[4]

All parameters in the constitution submodel are collected in Table II. Four are based on molecular weights: that of the aromatic nucleus, MW_A, is used to normalize those of labile bridges (MW_B/MW_A), char links (MW_C/MW_A), and peripheral groups (MW_P/MW_A). The tabulated values show that nuclei become more massive in coals of higher rank, and both the labile and refractory connections among them become smaller. The proportion of intact links in the whole coal, p(0), follows the tendency in the pyridine extract yields (in Table I) to remain constant for ranks through hv bituminous. It then rises precipitously for coals of higher ranks, consistent with their smaller extract yields because structures which are more tightly interconnected have fewer smaller fragments to be extracted. The fraction of labile bridges among intact links, $F^b(0)$, decreases from its value of unity for lignites in proportion to the carbon content. The values in Table II for carbon contents below 85% are based on the regression reported previously.[4] However, the sample population for that regression had few low volatility samples, whose total and tar yields were badly scattered. Based on the yields for the 4 samples in Chen and Niksa's study, the last 6 entries in Table II are given by $F^b(0) = 0.096 - 0.031(\%C, daf)$. In the future, this regression will be used for all carbon contents over 86%.

The selectivity coefficient between scission and spontaneous char condensation, ν_B, also varies with rank. Since crosslink formation has been clearly related to CO_2 evolution,[9] the values of ν_B are proportional to O/C ratios, but only for values below 0.2 or for carbon contents less than 83%. The latter restriction is consistent with the fact that precursors to CO_2 are either carboxyclic acid or ketone functionalities, which are present only in coals having lower carbon contents. The former restriction is based on data correlations for the low carbon-content samples in this study. (Our previous evaluation included no coals with such low carbon contents.)

Regarding the reaction rate parameters, those for recombination and peripheral group elimination and the expression for the saturated vapor pressure of tar precursors, P^{SAT}, are identical to values reported previously, and fixed for all coal types. The mean activation energy for bridge decomposition is also at its former value. But the frequency factor, A_B, and std. dev. in the bridge energy rate, σ, have been generalized in correlations with the carbon content, based on the correlations of transient weight loss presented below. Whereas these parameter correlations assign the same values reported previously for hv bituminous coals,[3] they prescribe significantly faster reaction rates at low temperatures for coals of lower rank. However, for ranks above hv bituminous, the bridge decomposition rates vary very little.

In the simulations reported below, the operating conditions of temperature, heating rate, and/or time were varied to match those in the experiments, while all coal properties and rate constants were specified according to Table II. A simulation of each thermal history requires from 2 to 5 minutes on a 386 personal microcomputer operating at 20 MHz, with an 8-Bit Fortran compiler.

RESULTS

Figures 1 and 2 present comparisons among the predicted and measured values of ultimate weight loss and tar yields, respectively. The measurements at 725K/s were taken for a 10 s reaction period at temperatures from 900 to 1100K. Simulations are based on the same heating rate and 5 s at 1000K, which is long enough to simulate complete devolatilization. The predictions are within experimental uncertainty for coals across the rank spectrum, except for the 1520 lignite and the 1516 low volatile bituminous. The latter discrepancy is especially difficult to rationalize because the prediction for 15,000 K/s with a virtually identical sample in Chen and Niksa's data is nearly exact.

Similarly, the significant enhancements in weight loss due to the 20-fold increase in heating rate in this data set are predicted within experimental uncertainty for all coal types.

Predicted tar yields in Fig. 2 are also quantitatively accurate, and there are no systematic deviations with coal rank. FLASHCHAIN also predicts that tar yields are substantially enhanced with faster heating, in accord with the observed behavior of all bituminous samples. Considering that 70% of the predictions in Figs. 1 and 2 (denoted by circles) are based on the parameters identified with an independent data base, these results also demonstrate that the ultimate analysis is the only coal-specific input required for accurate ultimate yields with FLASHCHAIN. The additional data on low volatility samples and the extended correlation for $F^b(0)$ appear to expand the range of rank which can be accurately simulated.

In addition to transient weight loss, this model accurately predicts the temperature dependence of ultimate yields, as seen in Figs. 3 and 4. Simulated transient weight loss is based on heatup at 800 K/s, whereas ultimate yields are based on heatup at 725 K/s, followed by 10 s isothermal reaction periods at the indicated temperatures. In Fig. 3 for the lignite (1443), these three quantities are correlated within experimental uncertainty at all temperatures. In Fig. 4, ultimate weight loss for an hvA bituminous sample (1499) is reliably correlated, but calculated tar yields are high by 4 wt%. Data from this coal also validates the calculated transient weight loss through 1000K. Unfortunately, the current data base can only be used to evaluate transient predictions for ranks through hv bituminous.

DISCUSSION

Predicting the ultimate weight loss and tar yields from any coal type is treated here as a matter of distinguishing aliphatic, heteroatomic, and aromatic constituents, rendering functional groups superfluous. In its submodel for coal constitution, FLASHCHAIN introduces the segregation of all oxygen and aliphatics into labile bridges and peripheral groups, and all aromatics and nitrogen into char links and aromatic nuclei. This crucial partitioning is implemented with balances based on the ultimate analysis, carbon aromaticity, and aromatic carbon number per monomeric unit. (Proton aromaticity is also included but found to be inconsequential.) The predictions reported here demonstrate that the ultimate analysis is the only coal-specific input needed with this theory. Regression values of all other inputs are the basis for accurate predictions, for reasons identified in our previous sensitivity study.[4] Now that the population for these regressions has been expanded by the addition of a few lignites and several low volatility coals, predictions can be generated for virtually any coal sample. This extension paves the way for examinations of extensive literature data for coal rank effects, now underway.

Regarding transient behavior, FLASHCHAIN reveals a new basis for interpreting and understanding the factors underlying the transient devolatilization of any coal type. FLASHCHAIN now incorporates this tendency through newly-identified correlations of the frequency factor and variance in the energy distribution for bridge decomposition with carbon content. From a practical standpoint, this approach yields reliable predictions for ranks from lignites through hv bituminous, but extensions to low volatility samples must await additional transient data.

From a mechanistic standpoint, inferences based on the trends in these rate constants should be closely circumscribed. Neither FLASHCHAIN nor any other current model includes the types of reaction mechanisms which can associate specific functionalities and reaction channels with the observed tendencies. There is, nevertheless, one obvious implication. In so far as oxygen content diminishes with increasing coal rank, the variations suggest that oxygenated species accelerate reaction rates during the early stages, as expected for any free-radical chain mechanism among hydrocarbons. Indeed, CO_2 and H_2O are major products during the initial stages.[6] Oxygenated species are also implicated in the broadening of the temperature range for devolatilization with decreasing rank, in that CO is always a major product of the latest stages of devolatilization.[6]

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Table I. Coal Properties

Sample	%C, daf	H/C	(O+S)/C	f_a'	AC/Cl	MW_{MON}	Y_{PYR}	MW_G
1443	66.5	.931	.306	.493	9.7	356	26	26.5
1520	69.0	.877	.271	.533	10.6	348	26	26.5
1488C	69.5	.863	.260	.541	10.8	345	26	26.5
1493C	74.1	.858	.136	.614	12.5	329	26	26.3
1493	75.5	.798	.179	.637	13.1	326	26	25.6
1499	79.9	.825	.122	.706	14.7	312	26	23.7
1451C	82.5	.815	.077	.748	15.7	305	26	22.5
1451	84.0	.803	.079	.772	16.2	300	26	21.8
1516	87.4	.614	.055	.826	17.5	291	26	20.3
CBMC	87.5	.759	.021	.827	17.5	290	26	20.2
1516C	88.7	.676	.018	.846	18.0	288	21.6	19.7
1521C	89.6	.643	.019	.861	18.3	285	14.8	19.3
1508C	89.9	.614	.035	.865	18.4	284	12.5	19.2
1468	94.3	.237	.024	.935	20.1	276	0	17.2

*The suffix "C" denotes samples of Chen and Niksa;[6] all others are Friehaut and Proscia's.[5]

Table II. Structural Model Parameters

Sample	MW_A	C_A	MW_B/MW_A	MW_C/MW_A	MW_S/MW_A	p(0)	$F^b(0)$	v_B	v_E
1443	125	9.7	1.859	.836	.511	.911	1.000	.150	2.40
1520	134	10.6	1.602	.721	.442	.911	1.000	.150	2.23
1488C	135	10.7	1.563	.704	.430	.911	0.983	.150	2.19
1493C	148	11.6	1.307	.588	.359	.911	0.858	.329	2.03
1493	152	11.9	1.258	.566	.347	.911	0.821	.202	2.05
1499	165	12.9	1.044	.470	.288	.911	0.702	.370	2.00
1451C	176	13.7	0.901	.406	.247	.911	0.632	.500	1.93
1451	180	14.1	0.838	.377	.230	.911	0.591	.500	1.90
1516	169	13.4	1.079	.485	.297	.911	0.329	.500	2.48
CBMC	182	14.2	0.886	.399	.243	.911	0.366	.500	2.19
1516C	183	14.4	0.866	.390	.239	.920	0.329	.500	2.21
1521	186	14.6	0.836	.376	.230	.937	0.301	.500	2.21
1508C	181	14.4	0.897	.404	.247	.943	0.291	.500	2.33
1468	178	14.5	1.005	.452	.097	1.000	0.154	.500	2.86

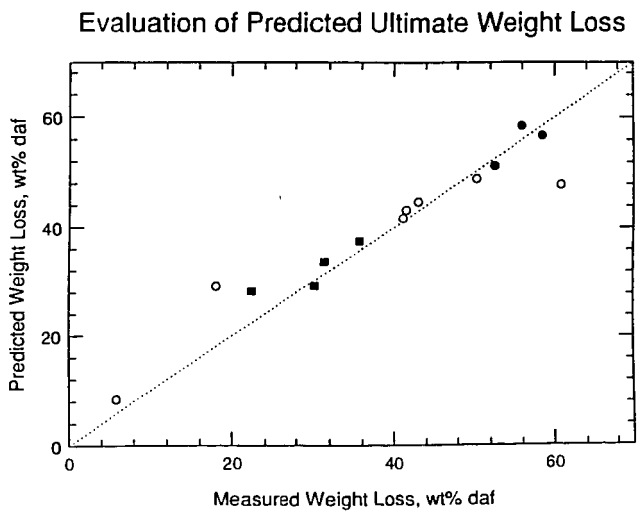

Figure 1. An evaluation of predicted weight loss for the coals in Table I versus measured values. Measured values were reported by Freihaut and Proscia[5] for atmospheric devolatilization for a heating rate of 725 K/s and 10 s at temperatures from 900 to 1100 K (open symbols); and by Chen and Niksa[6] for a heating rate of 15,000 K/s to a temperature high enough to achieve complete primary devolatilization (filled symbols). Predicted values are based on the parameters in Tables II and III and heatup at 725 K/s with 5 s at 1100 K and at 15000 K/s to 1300K. All cases denoted by circles are based solely on parameter values assigned for an independent data base.

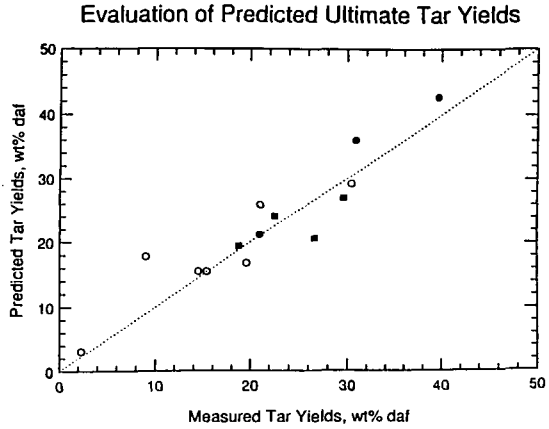

Figure 2. An evaluation of predicted ultimate tar yields for the coals in Table I versus measured values. Measured values were reported by Freihaut and Proscia[5] for atmospheric devolatilization for a heating rate of 725 K/s and 10 s at temperatures from 900 to 1100 K (open symbols); and by Chen and Niksa[6] for a heating rate of 15,000 K/s to a temperature high enough to achieve complete primary devolatilization (filled symbols). Predicted values are based on the parameters in Tables II and III and heatup at 725 K/s with 5 s at 1100 K and at 15000 K/s to 1300K. All cases denoted by circles are based solely on parameter values assigned for an independent data base.

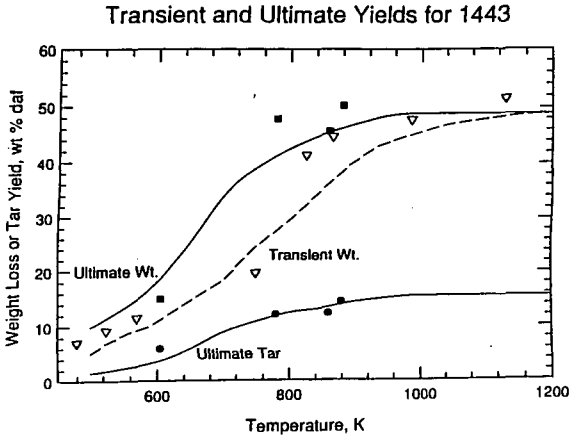

Figure 3. Comparisons between measured and predicted ultimate weight loss and tar yields and weight loss during transient heatup for a lignite (1443). Data were reported by Freihaut and Proscia[5] for a heating rate of 725 K/s and 10 s at the indicated temperatures, for ultimate values, and rates from 650 to 1250 K/s and nominal cooling rates from 1500 to 2000 K/s for the transient data. The respective simulations are based on identical conditions for the ultimate yields, and a heating rate of 800 K/s to the indicated temperatures without allowing for decomposition during cooling, which is negligible at such fast cooling rates.

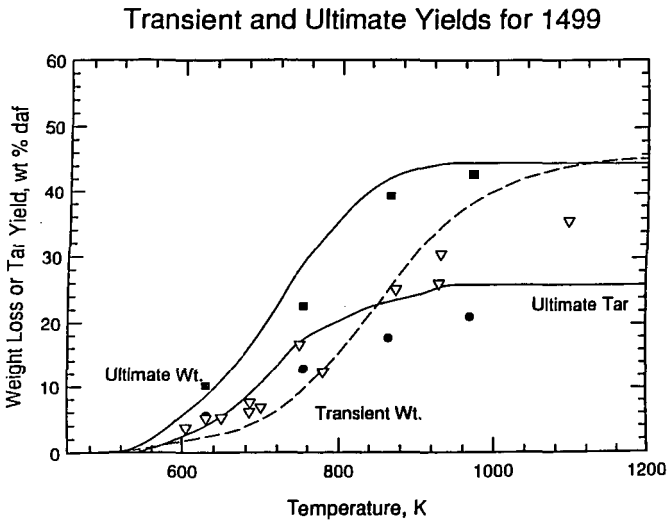

Figure 4. Comparisons between measured and predicted ultimate weight loss and tar yields and weight loss during transient heatup for an hvA bituminous coal (1443). Data were reported by Freihaut and Proscia[5] for a heating rate of 725 K/s and 10 s at the indicated temperatures, for ultimate values, and rates from 650 to 1250 K/s and nominal cooling rates from 1500 to 2000 K/s for the transient data. The respective simulations are based on identical conditions for the ultimate yields, and a heating rate of 800 K/s to the indicated temperatures without allowing for decomposition during cooling, which is negligible at such fast cooling rates.